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(54)

Thick film paste compositions for use with an aluminum nitride substrate.

(57)

A thick film paste composition adapted to be bonded onto an aluminum nitride substrate is provided which comprises (a) an electrical property regulating component present in an amount sufficient to control the electrical properties of said paste; (b) a lead free or low lead glass composition capable of bonding said electrical property regulating component to the surface of an aluminum nitride substrate, said glass composition including, in weight percent; and (c) an organic dispersion medium for said electrical regulating property component and said glass composition. A method of applying the thick film paste to an aluminum nitride substrate is also disclosed.

SiO₂..27.0 to 56.5; BaO..0 to 47.0; B₂O₃..4.5 to 25.0; PbO..0 to 18.0; ZnO..0 to 15.0; Al₂O₃..3.0 to 14.0; ZrO₂..0 to 3.0; MgO..0 to 8.0; CaO..0 to 12.0; F₂..0 to 3.0; K₂O..0 to 3.0; Na₂O..0-3.0; WO₃..0 to 4.0; Li₂O..0 to 4.0; wherein
BaO + PbO ≥ 15.0; ZnO + CaO + Al₂O₃ ≥ 5.0; CaO + MgO + BaO ≥ 7.0; CaO + MgO + ZrO₂ ≥ 1.0; ZrO₂ + CaO + BaO ≥ 7.0; K₂O + Na₂O + (PbO or BaO) ≥ 10.0.

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barium oxide plus lead oxide is present in an amount at least equal to about 15.0 percent, zinc oxide plus calcium oxide plus aluminum oxide is present in an amount at least equal to about 5.0 percent, calcium oxide plus magnesium oxide plus barium oxide is present in an amount at least equal to about 7.0 percent, calcium oxide plus magnesium oxide plus zirconium oxide is present in an amount at least equal to about 1.0 percent, zirconium oxide plus calcium oxide plus barium oxide is present in an amount at least equal to about 7.0 percent, and potassium oxide plus sodium oxide plus lead oxide or barium oxide is present in an amount at least equal to 10.0 percent; and (iii) an organic dispersion medium for the electrical property modifier component and the glass composition; and c) heating the so-applied paste composition to a temperature sufficient to cause the paste to become bonded to the aluminum nitride substrate.

Detailed Description Of preferred Embodiments

The present invention concerns a novel thick film paste composition which is adapted for use on an aluminum nitride substrate. Broadly, the paste composition includes (a) an electrical property modifier component, (b) a special lead free or low lead glass (i.e., generally contains 20 percent or less lead) binder which is capable of bonding to an aluminum nitride substrate, and (c) an organic vehicle or dispersing medium for the inorganic constituents of the paste.

As used herein the term "aluminum nitride substrate" is intended to mean a substrate containing in excess of 40 weight percent aluminum nitride.

One of the important features of the present invention is that by properly selecting the electrical property modifier component, the resultant paste can serve as either a conductor, a resistor or a dielectric. The specific material utilized to render the paste of the invention conductive, dielectric, or resistive is not critical per se. All that is required is that it produce the desired electrical properties in the final product. If the paste is to be electrically conductive, it is common to use a suitably conductive metal as the electrical modifier component; if the paste is to be resistive, ruthenium dioxide is generally employed; if the paste is to function as a dielectric, the composition can be used alone or a refractory oxide filler can be utilized. Since the use of these electrical property modifier materials is well known in the art, they will not be discussed hereinafter in detail.

The glass binders used in connection with the present invention is critical in that it must bond to aluminum nitride. Glasses which have been found to be exceptionally useful for this purpose include those containing the listed components within the ranges specified in Table 1.

TABLE 1
Compositional Range
(in weight %)

<u>Component</u>	<u>Compositional Range (in weight %)</u>
SiO ₂	27.0-56.5
BaO	0-47.0
B ₂ O ₃	4.5-25.0
PbO	0-18.0
ZnO	0-15.0
Al ₂ O ₃	3.0-14.0
ZrO ₂	0-3.0
MgO	0-8.0
CaO	0-12.0
F ₂	0-3.0
K ₂	0-3.0
Na ₂ O	0-3.0
WO ₃	0-4.0
LiO ₂	0-4.0

Wherein:

- (1) barium oxide plus lead oxide is present in an amount at least equal to about 15.0 percent,
- (2) zinc oxide plus calcium oxide plus aluminum oxide is present in an amount at least equal to about 5.0 percent,
- (3) calcium oxide plus magnesium oxide plus barium oxide is present in an amount at least equal to about 7.0 percent,
- (4) calcium oxide plus magnesium oxide plus zirconium oxide is present in an amount at least equal to about

TABLE 3
Compositional Range
(in weight %)

Component	Glass D	Glass E	Glass F	Glass G
SiO ₂	36-43	40-48	28-38	50-56.5
BaO	20-25	8-16	35-40	0-5
B ₂ O ₃	10-16	6-11	7-20	3-8
PbO	---	8-18	---	10-18
ZnO	9-14	0-5	---	---
Al ₂ O ₃	3-8	3-7	8-14	7-11
ZrO ₂	0-3	0-3	0-2	---
MgO	0-6	0-6	---	---
CaO	---	2-8	---	7-12
F ₂	---	0-3	---	---
K ₂ O	---	---	---	0-3
Na ₂ O	---	---	---	---
WO ₃	---	---	0-4	---
LiO ₂	---	0-3	---	---
	(a)	(b)	(c)	(d)

(a) In Glass D, zirconium oxide plus magnesium oxide is present in an amount of at least about 1.0 percent.

(b) In Glass E, zinc oxide plus calcium oxide is present in an amount of at least 5.0 percent, magnesium oxide plus calcium oxide is present in an amount of at least 5.0 percent, zinc oxide plus calcium oxide is present in an amount of at least 3.0 percent, fluorine plus lead oxide is present in an amount of at least 9.0 percent, lithium oxide plus lead oxide is present in an amount of at least 10.0 percent.

(c) In Glass F, zirconium oxide plus tungsten oxide is present in an amount of at least 1.0 percent.

(d) In Glass G, barium oxide plus calcium oxide is present in an amount of at least 9.0 percent, potassium oxide plus calcium oxide is present in an amount of about at least 8.0 percent.

Many inert liquids can be used as the dispersing medium in the practice of the present invention. Water or any one of various organic liquids, with or without thickening and/or stabilizing agents and/or other common additives can be used as the dispersing medium. Exemplary of the organic liquids which can be used are the aliphatic alcohols; esters of such alcohols, for example, the acetates and propionates; terpenes such as pine

Example II
(Dielectric Formulation)

<u>Component</u>	<u>Weight %</u>
Glass Binder*	47.6
Electrical Property Modifier	
(A) Al ₂ O ₃	13.6
(B) Cordierite	6.8
Organic Vehicle	32.0

*Glass Binder Composition

<u>Component</u>	<u>Weight Percent</u>
SiO ₂	38.9
BaO	23.9
B ₂ O ₃	13.4
ZnO	12.0
Al ₂ O ₃	5.0
ZrO ₂	1.5
MgO	5.3

A dielectric thick film paste consisting of the foregoing ingredients was prepared and applied to an aluminum nitride substrate in the same manner as described in Example I.

Upon testing, it was observed that the paste was adherently bonded to the substrate. The dielectric properties of the paste were as follows:

Insulation Resistance - 1.5-7.0 x 10¹²ohms

Dielectric Constant - 7.0-7.5

Adhesion - 7000-8000 psi

Breakdown Voltage - greater than 400 Volts per mil

Example III

(Resistor Formulation)

<u>Component</u>	<u>Weight %</u>
Noble Metal Containing Conductive Phase	37.7
Glass Binder*	30.4
Refractory Filler Oxides	7.4
Organic Vehicle	24.5

The Glass Binder* utilized was the same as that employed in Example I.

A resistor thick film paste consisting of the foregoing ingredients was prepared and applied to an aluminum nitride substrate in the same manner as described in Example I.

Upon testing it was observed that the paste was adherently bonded to the substrate. The resistor properties of the paste were as follows:

Sheet Resistivity (Ps) - 10 Ohms/square

<u>Component</u>	<u>Compositional Range (in weight percent)</u>	
SiO ₂	37-56.5	
BaO	0-24	5
B ₂ O ₃	4-14	
PbO	0-18	
ZnO	0-12.2	
Al ₂ O ₃	3-10	10
ZrO ₂	0-3	
MgO	0-6	
CaO	0-8	
F ₂	0-3	15
K ₂ O	0-3	
Na ₂ O	0-3	
LiO ₂	0-3	20

3. The thick film composition of claim 1 wherein said glass composition includes

<u>Component</u>	<u>Compositional Range (in weight percent)</u>	
SiO ₂	38-45	30
BaO	10-24	
B ₂ O ₃	7-14	
PbO	0-17	
ZnO	5-12.2	35
Al ₂ O ₃	3-8	
ZrO ₂	0-3	
MgO	0-6	
CaO	0-7	40
F ₂	0-3	
LiO ₂	0-3	

4. The thick film composition of claim 1 wherein said glass composition includes

<u>Component</u>	<u>Compositional Range (in weight percent)</u>	
SiO ₂	28-45	
BaO	20-40	
B ₂ O ₃	7-20	55
Al ₂ O ₃	2-14	
ZrO ₂	0-3	
MgO	0-8	
WO ₃	0-4	60

5. The thick film composition of claim 1 wherein said electrical property modifier component is a material which renders said composition electrically conductive.

- percent; and
- (c) an organic dispersion medium for said electrical property modifier component and said glass composition.
12. A thick film paste composition which can be bonded to an aluminum nitride substrate, comprising
- (a) an electrical property modifier component present in an amount sufficient to regulate the electrical properties of said paste; 5
 - (b) a lead free or low lead glass composition capable of bonding to the surface of an aluminum nitride substrate, said glass composition including, in weight percent, from about 40.0 to about 48.0 percent silicon dioxide, from about 8.0 to about 16.0 percent barium oxide, from about 6.0 to about 11.0 percent boron oxide, from about 8.0 to about 18.0 percent lead oxide, from about 0 to about 5.0 percent zinc oxide, from about 3.0 to about 7.0 percent aluminum oxide, from about 0 to about 3.0 percent zirconium oxide, from about 0 to about 6.0 percent magnesium oxide, from about 2.0 to about 8.0 percent calcium oxide, from 0 to about 3.0 percent fluorine, and from 0 to about 3.0 percent lithium oxide, wherein zinc oxide plus calcium oxide is present in an amount of at least 5.0 percent, magnesium oxide plus calcium oxide is present in an amount of at least 5.0 percent, zinc oxide plus calcium oxide is present in an amount of at least 3.0 percent, fluorine plus lead oxide is present in an amount of at least 9.0 percent and lithium oxide plus lead oxide is present in an amount of at least 10.0 percent; and 10
 - (c) an organic dispersion medium for said electrical property modifier component and said glass composition. 15
13. A thick film paste composition which can be bonded to an aluminum nitride substrate, comprising
- (a) an electrical property modifier component present in an amount sufficient to regulate the electrical properties of said paste; 20
 - (b) a lead free or low lead glass composition capable of bonding to the surface of an aluminum nitride substrate, said glass composition including, in weight percent, from about 28.0 to about 38.0 percent silicon dioxide, from about 35.0 to about 40.0 percent barium oxide, from about 7.0 to about 20.0 percent boron oxide, from about 8.0 to about 14.0 percent aluminum oxide, from 0 to about 2.0 percent zirconium oxide, and from about 0 to about 4.0 percent tungsten oxide, wherein zirconium oxide plus tungsten oxide is present in an amount of at least 1.0 percent; and 25
 - (c) an organic dispersion medium for said electrical property modifier component and said glass composition. 30
14. A thick film paste composition which can be bonded to an aluminum nitride substrate, comprising
- (a) an electrical property modifier component present in an amount sufficient to regulate the electrical properties of said paste;
 - (b) a lead free or low lead glass composition capable of bonding to the surface of an aluminum nitride substrate, said glass composition including, in weight percent, from about 50.0 to about 56.5 percent silicon dioxide, from about 0 to about 5.0 percent barium oxide, from about 3.0 to about 5.0 percent boron oxide, from about 10.0 to about 18.0 percent lead oxide, from 7 to about 11.0 percent aluminum oxide, from about 7 to about 12.0 percent calcium oxide, and from about 0 to about 3.0 percent potassium oxide, wherein barium oxide plus calcium oxide is present in an amount of at least 9.0 percent, potassium oxide plus calcium oxide is present in an amount of at least 8.0 percent; and 35
 - (c) an organic dispersion medium for said electrical property modifier component and said glass composition. 40
15. A method of adherently depositing a thick film paste on an aluminum nitride substrate which comprises
- a) providing an aluminum nitride substrate;
 - b) applying a thick film paste composition to said aluminum nitride substrate, said paste composition including 45
 - (i) an electrical property modifier component present in an amount sufficient to control the electrical properties of said paste;
 - (ii) a lead free or low lead glass composition capable of bonding to the surface of an aluminum nitride substrate, said glass composition including, in weight percent, from about 27.0 to about 56.5 percent silicon dioxide, from about 0 to about 47.0 percent barium oxide, from about 4.5 to about 25.0 percent boron oxide, from about 0 to about 18.0 percent lead oxide, from about 0 to about 15.0 percent zinc oxide, from about 3.0 to about 14.0 percent aluminum oxide, from about 0 to about 3.0 percent zirconium oxide, from about 0 to about 8.0 percent magnesium oxide, from about 0 to about 12.0 percent calcium oxide, from about 0 to about 3.0 percent fluorine, from about 0 to about 3.0 percent potassium oxide, from about 0 to about 3.0 percent sodium oxide, from about 0 to about 4.0 percent tungsten oxide, and from about 0 to about 4.0 percent lithium oxide, wherein barium oxide plus lead oxide is present in an amount at least equal to about 15.0 percent, zinc oxide plus calcium oxide plus aluminum oxide is present in an amount at least equal to about 5.0 percent, calcium oxide plus magnesium oxide plus barium oxide is present in an amount at least equal to about 7.0 percent, calcium oxide plus magnesium oxide plus zirconium oxide is present in an amount at least equal to about 1.0 percent, zirconium oxide plus calcium oxide plus barium oxide is present in an amount at least equal to about 7.0 percent, and potassium oxide plus sodium oxide plus lead oxide or barium oxide is present in an amount at least equal to 10.0 percent; and 50
 - (iii) an organic dispersion medium for said electrical property modifier component and said glass 55



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 88308023.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP - A1 - O 132 810 (E.I.DU PONT) * Claims; examples I, XVIII * --	1-6, 11-16, 18, 19	H 01 B 1/16 H 01 B 3/08 H 01 C 7/00
A	EP - A2 - O 153 737 (TOSHIBA) * Abstract; claims; page 9, lines 1-16; page 14, table 2 * --	1, 11-17, 19	H 01 L 49/02 //C 03 C 8/02
A	US - A - 4 540 673 (TAKEDA et al.) * Abstract *	1, 11-14	
A	GB - A - 1 251 766 (E.I.DU PONT) * Claims 1, 2, 4-6, 120, 13, 14; page 2, line 12 - page 2, line 6 * ----	1, 11-14	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			H 01 B H 01 C 7/00 H 01 L C 03 C C 04 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 22-11-1988	Examiner KUTZELNIGG
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